

The Fundamental and Exploratory Research Program (FERP) within ESD covers fundamental earth sciences research conducted in support of the Department of Energy's science mission. This mission includes research in the natural sciences to provide a basis for new and improved energy technologies and for understanding and mitigating the environmental impacts of energy development and use. FERP also includes exploratory research in important new energy and environmental topics conducted under the Laboratory Directed Research and Development (LDRD) program. The scientific insights and breakthroughs achieved in FERP often become the underpinnings for projects that support DOE's applied research and development program offices.

The basic earth sciences research program at Berkeley Lab has focused on four broad earth sciences problems:

1. Fundamental studies of chemical and mass transport in geologic media—with special reference to predictive modeling of multiphase, multicomponent, nonisothermal fluid flow in saturated and unsaturated fractured rock
2. The development of new isotopic techniques for understanding the nature of a broad range of global processes—from the relatively short-term effects of natural fluid migration in the crust to longer-term (i.e., 10–20 thousand years) global climate variations
3. Imaging the subsurface—fundamental studies in the propagation of seismic/acoustic and broadband electromagnetic waves through geologic media, with emphasis on new computational techniques for high-resolution imaging of near-surface and crustal structures (such as possible fracture flow paths) and for inferring the types of fluids present in pores and fractures
4. The development of a nanogeoscience center—The defining aspect of nanogeoscience is its interconnecting chemical



Research Program

FUNDAMENTAL AND EXPLORATORY RESEARCH PROGRAM

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pathways, uniting aspects of natural inorganic, organic, and biological processes with specific interactions and mechanisms common to mineral surfaces, small particles, and particle aggregates. The focus is on various combinations of several key topics, defined with respect to important specific problems within the DOE complex, and aimed at elucidation of fundamental scientific problems and reaction pathways. Work in this field is necessarily diverse and complex, and requires the close collaborations of investigators having both a wide knowledge base—encompassing geochemistry, colloid chemistry, surface chemistry, materials science, biochemistry and physical chemistry—and a strong interest in shared goals, utilizing a team effort. In bringing separate tasks together under one umbrella, efforts can now be combined with a grand synergy that would be difficult to achieve with separate subprojects operated in different locations without temporal congruence. The new laboratory and task structure will function as a focus for all relevant environmentally related nanoscience at LBNL, and also provide a superb location for the development of top-flight scientists in this field.

Results from these research endeavors have had a major impact on applied energy, carbon management/climate change, environmental, and radioactive waste management programs. Current research projects are briefly described here.

CHEMICAL AND MASS TRANSPORT INVESTIGATIONS

Current research in this area is focused on nanoparticle and colloid transport in unsaturated porous media and rock fractures, chemical transport in structure porous media, unsaturated fast flow in fractured rock, and production and evaluation of coupled processes for CO₂ in aquifers. The nanoparticle research focuses on the mobile fractions and natural abundance in soils. Also studied is the rate of infiltration in the unsaturated zone, an important issue in studying and defining the driving forces and boundary conditions in the containment and cleanup of contaminants in the subsurface. Also being researched are interfacial reactions such as at quartz/water

interfaces and the intergranular diffusion in uranium and in sand. Another study has focused on the use of x-ray absorption and diffraction methods to study sorption processes.

ISOTOPE GEOCHEMISTRY

The Center for Isotope Geochemistry (CIG) is a state-of-the-art analytical facility established in 1988 to measure the concentrations and isotopic compositions of elements in rocks, minerals, and fluids in the earth's crust, atmosphere, and oceans. Fundamental research conducted at this center is directed at finding new ways to use isotopic information to study earth processes, such as long-term climate changes, and at predicting the chemical transport of mantle-derived or deep crustal fluids as they move through the crust.

One of the major problems being studied at CIG is how to estimate fluid-solid reaction rates in natural-groundwater higher-temperature geothermal conditions, particularly as these rates affect mineral dissolution and secondary mineral precipitation. ESD researchers are developing novel ways of estimating reaction rates by using isotopic tracers (primarily strontium, but also uranium and neodymium) to determine solid-fluid exchange rates in various natural situations. Scientists are able to derive the "reaction length," a parameter that depends on the ratio of isotope transport by diffusion and advection to the reaction rate. The ultimate objective is to understand the microscopic (as well as pore-scale and mesoscale) characteristics of natural systems that have been characterized in terms of "field scale" reaction-rate measures. An intermediate goal is to establish empirically the natural range of fluid-solid reaction rates. Examples are the U-Th/He geochronology of young volcanic rock, understanding and predicting the microbial degradation of chlorinated solvents with carbon isotopes, and using xenon isotopes to study buried waste.

ADVANCED COMPUTATION FOR EARTH IMAGING

The Center for Computational Seismology (CCS) was created in 1983 as the Berkeley Lab and UC Berkeley nucleus for seismic research related to data processing, advanced imaging, and visualization. In recent years, a great deal of cross-fertilization between seismologists and other geophysicists and hydrogeologists has developed within the division, resulting in collaborations on a

wide variety of fundamental imaging problems. A primary thrust in this research has been to jointly develop seismic and electrical methods for understanding fluid flow and properties within the subsurface. In addition, fundamental studies on improved inversion and modeling of complex media in 3-D are being carried out to analyze such effects as matrix heterogeneity fluid flow and anisotropy. Applications range from small-scale environmental problems to oil and gas reservoirs.

ROCK PHYSICS

A variety of rock and soil science experiments are being conducted through ESD's Geoscience Measurements Facility, which supports both field and laboratory work. In one new laboratory project, researchers are studying the compaction and fracturing of weakly cemented granular rocks. This study examines the effect of micromechanical properties of weak granular rock on macroscopic properties such as load-displacement response, ultimate strength, and failure mode. In a second study, a fundamental investigation of scattering and intrinsic attenuation of seismic waves in rock with heterogeneous distributions of fluids and gas is being conducted. This research represents a departure from past rock-physics studies on seismic attenuation, in that the emphasis here is not a detailed study of a specific attenuation mechanism, but rather to investigate theoretical and laboratory methods for obtaining separate estimates of scattering and intrinsic attenuation in rock with heterogeneous pore-fluid distributions.

FUNDING

Funding for research in the Fundamental and Exploratory Research Program comes from a variety of sources. These include (primarily) the U.S. Department of Energy, through the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences; the Office of Biological and Environmental Research; the Assistant Secretary for Fossil Energy, Office of Natural Gas and Petroleum Technology, National Petroleum Technology Office, Natural Gas and Oil Technology Partnership; and the Office of Environmental Management Science Program. Funding is also provided by the Laboratory Directed Research and Development Program (LDRD) at Berkeley Lab.

ISOTOPE FRACTIONATION BY DIFFUSION IN LIQUID WATER

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RESEARCH OBJECTIVES

Solute isotopic compositions have emerged as important indicators of geophysical and biogeochemical processes. The best-known isotopic geochemistry methods use various isotopic ratios as “signatures” of biological processes, geological time, and paleoclimatic conditions. Less widely recognized is the fact that diffusion in liquid water, a transport process ubiquitous in the biogeosphere, has its own isotopic signature, which results from the isotopic mass dependence of solute diffusion coefficients. We have applied molecular dynamics simulations to investigate this mass dependence for both neutral and ionic solutes in liquid water (Bourg and Sposito, 2007a,b), to determine its potential influence on solute isotopic compositions.

APPROACH

We carried out 8 ns molecular dynamics simulations of the motions of a single solute ion or molecule, immersed in 215 to 550 water molecules and moving in a periodically replicated simulation cell (Figure 1) maintained at the appropriate density of liquid water. In such simulations, molecular positions and velocities are calculated from the Newton-Euler equations of motion for a set of molecules (with freely chosen atomic masses) and interatomic potentials. We repeated each simulation with the solute isotopic mass varied systematically over a broad range (2 to 132 Da) to determine the mass dependence of the solute diffusion coefficient, which was calculated by a standard quadrature involving the velocity autocorrelation function.

ACCOMPLISHMENTS

We determined the isotopic mass dependence for the diffusion coefficients of five noble gases (He, Ne, Ar, Kr, Xe), four monovalent cations (Li^+ , Na^+ , K^+ , Cs^+), a monovalent anion (Cl^-) and a divalent cation (Mg^{2+}). All solutes exhibited an inverse power-law relation between their diffusion coefficients and isotopic mass, as proposed recently by our collaborator Frank M. Richter (University of Chicago) on empirical grounds. The solute isotopic mass dependence increased in the order: divalent ion < monovalent ions < noble gases. Simulation results obtained for Li^+ , Cl^- and Mg^{2+} and for the major isotopes of the noble gases He, Ne, Kr, and Xe agreed with available experimental data, thus confirming the accuracy of our simulation methods (Bourg and Sposito, 2007a,b).

SIGNIFICANCE OF FINDINGS

Our results for the noble gases have particularly important geochemical implications, because of the paucity of experimental data on noble gas diffusion in liquid water and because of the widespread use of dissolved

noble gases in paleoclimatic and groundwater hydrology studies. More specifically, we found that the isotopic mass dependence of noble gas diffusion coefficients in water is significantly smaller than that predicted by a kinetic-theory model used extensively—but never tested directly—in noble gas geochemistry. This finding offers a major challenge to the conclusions reached in many recent publications on paleoclimatic reconstructions and groundwater hydrology.

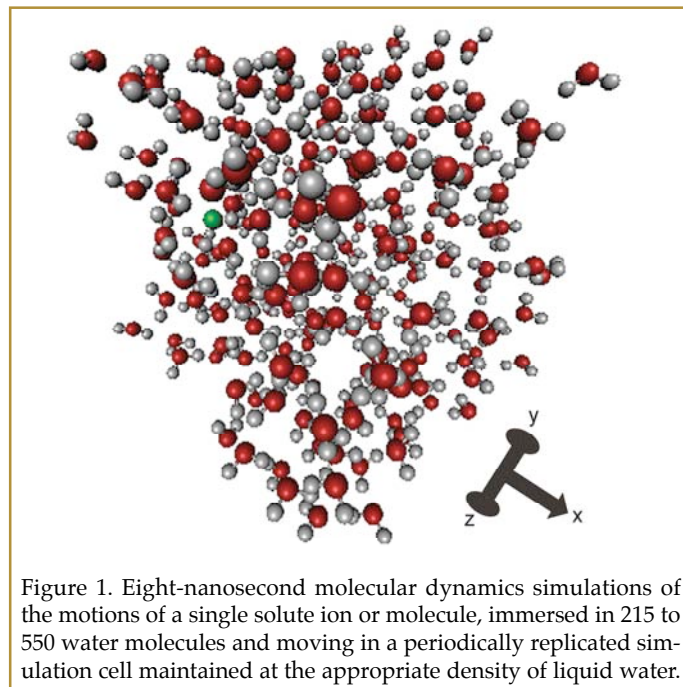


Figure 1. Eight-nanosecond molecular dynamics simulations of the motions of a single solute ion or molecule, immersed in 215 to 550 water molecules and moving in a periodically replicated simulation cell maintained at the appropriate density of liquid water.

RELATED PUBLICATION

- Bourg, I.C., and G. Sposito, Molecular dynamics simulations of kinetic isotope fractionation during the diffusion of ionic species in liquid water. LBNL-61833. *Geochimica et Cosmochimica Acta* (in press), 2007a.
- Bourg, I.C., and G. Sposito, Isotopic mass-dependence of noble gas diffusion coefficients in water. *Physical Review Letters* (submitted), 2007b.

ACKNOWLEDGMENTS

This research was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. Our computations used resources of the National Energy Research Scientific Computing Center (NERSC) at Berkeley Lab, which is also supported by DOE under Contract No. DE-AC02-05CH11231.

USING ISOTOPES TO TRACK SPRING 2002 DUST STORMS OVER HEFEI, CHINA

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RESEARCH OBJECTIVES

Aerosols—small particles less than 50 microns lofted into the atmosphere—can travel on winds vast distances across the globe. Such fine particulates can include soil-derived dust, biogenic material, sea spray, and industrial pollutants. Far-traveled aerosols can affect air quality, the way the atmosphere absorbs or reflects the sun's heat, and cloud formation. Analysis of elemental data for aerosols collected over California has identified a persistent Asian soil dust component that peaks with Asian dust storm events. Such Asian-derived aerosols can also bring with them industrial pollutants that can affect air quality in California. To further understanding of intercontinental transport of aerosols, we undertook a study of the isotopic composition of aerosols as a fingerprint for their sources and evolution. As a basis for our study of aerosols collected in California, we have analyzed samples from Hefei, China, as a representation of Asian sources.

APPROACH

We use isotopic fingerprinting based on the isotopic composition of Sr, represented by the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. Through the decay of ^{87}Rb over geologic time, the $^{87}\text{Sr}/^{86}\text{Sr}$ of earth materials differs, depending on their geologic history and $^{87}\text{Rb}/^{86}\text{Sr}$. We combined Sr isotopic data with elemental data both determined from daily 24-hour samples of PM_{2.5} (particles <2.5 microns in diameter) collected in Hefei, China. The collection period was during spring 2002, concurrent with changing weather conditions, including a series of major dust storms arising from deserts in western China. Prior to destructive isotopic analysis, the elemental composition of the particulate matter (PM) was determined by synchrotron-XRF analysis performed at the ALS at Lawrence Berkeley National Laboratory. The PM was then dissolved off the filters and analyzed for Sr isotopic composition and concentrations of K, Rb, Sr, and Nd. We used a modeling program HYSPLIT provided by the National Oceanographic and Atmospheric Administration to calculate air-mass back trajectories to support interpretations of aerosol sources.

ACCOMPLISHMENTS

We analyzed filters covering April to the beginning of May 2002. Comparison of the time series for $^{87}\text{Sr}/^{86}\text{Sr}$ (Figure 1, top) with calcium and silicon concentrations (not shown) indicates a correspondence between high-dust days and highs in $^{87}\text{Sr}/^{86}\text{Sr}$, while lows are associated with precipitation events. Plotting Sr isotopic composition against various elemental ratios provides identification of end-member components in the mixture of particulates in the sample. For example, Figure 1 (bottom) shows $^{87}\text{Sr}/^{86}\text{Sr}$ vs. Ca/Sr. This plot indicates that the PM_{2.5} samples represent variable mixing between a high $^{87}\text{Sr}/^{86}\text{Sr}$ end-member (desert dust), and at least two different low $^{87}\text{Sr}/^{86}\text{Sr}$ components, one representing

marine aerosol and another representing "local" China sources influenced by urban pollution. Samples labeled with dates have a significant component of marine aerosol Sr, consistent with weather and air mass back-trajectories.

SIGNIFICANCE OF FINDINGS

This study demonstrates that the components of aerosol mixtures can be traced to their sources using a combination of Sr isotopic data and elemental data. The results we presented here yield constraints on the isotopic signatures of aerosols derived from China that include both desert dust and pollution sources. This provides us a starting-point compositional signature for determining the contribution of Asian-sourced materials to aerosols in California and evaluating their role in air quality.

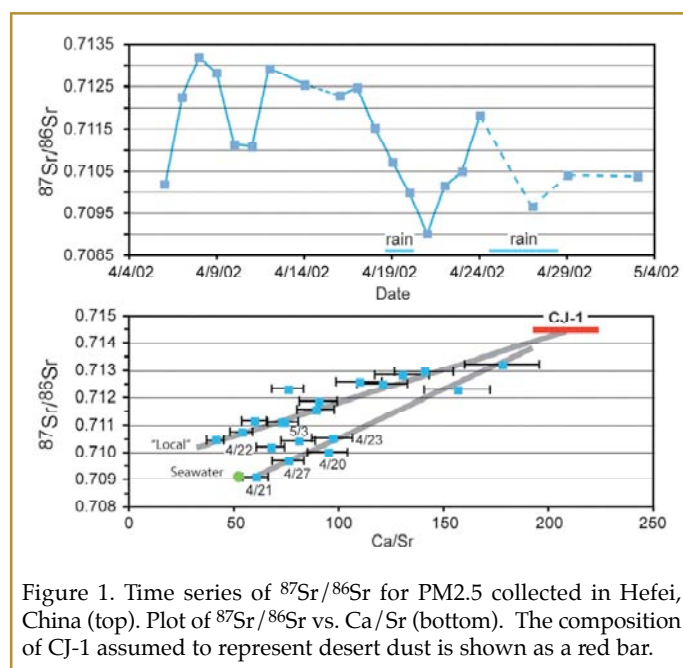


Figure 1. Time series of $^{87}\text{Sr}/^{86}\text{Sr}$ for PM_{2.5} collected in Hefei, China (top). Plot of $^{87}\text{Sr}/^{86}\text{Sr}$ vs. Ca/Sr (bottom). The composition of CJ-1 assumed to represent desert dust is shown as a red bar.

RELATED PUBLICATION

Christensen, J.N., S.S. Cliff, R.A. Van Curen, K.D. Perry, and D.J. DePaolo, Tracking intercontinental dust transport with radiogenic isotopes: Hefei, China to California, Spring 2002. AGU 2006 Fall Meeting. Eos Transactions American Geophysical Union, Abstract A43B-0138, 2006.

ACKNOWLEDGMENTS

This work was supported by Laboratory Directed Research and Development (LDRD) funding from Berkeley Lab, provided by the Director, Office of Science, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.



INVESTIGATING MINERAL PRECIPITATION MECHANISMS WITH Ca ISOTOPES

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RESEARCH OBJECTIVES

Precipitation of minerals from aqueous solution is often assumed to be a well-understood phenomenon. But the precise mechanisms by which dissolved ions are attached to mineral surfaces to allow solid crystals to grow from solution are both complex and poorly characterized, even for familiar minerals. Recent advances have been made using micro-imaging techniques such as atomic force microscopy and synchrotron x-rays, and insights are being gained from molecular dynamics and *ab initio* calculations. The results of these studies tend to emphasize the complexity of the precipitation process, the variability as a function of conditions such as oversaturation and fluid chemistry, and the evidence that chemical equilibrium is not maintained during the process. In the geosciences, the departures from equilibrium attending mineral precipitation are particularly important, because mineral properties such as isotopic composition and trace-element content are used to reconstruct past Earth climate and ocean chemistry, and the assumption is commonly made that the minerals (such as calcite) form at equilibrium or near-equilibrium conditions.

APPROACH

We are investigating the use of isotopes to study processes at mineral surfaces. This approach is based on chemical differences between isotopic species—their mobility in solution, rates of attachment and detachment from mineral surfaces, and thermodynamic affinity in different chemical bonding environments. We measure Ca isotope ratios in the minerals calcite (CaCO_3) and gypsum (CaSO_4), which are formed by precipitation from aqueous solutions in soils, lakes, and the oceans. Ca isotopes are ideal because it appears that all of the fractionation produced in the precipitation process is caused by transport at the mineral-water interface.

ACCOMPLISHMENTS

To determine the equilibrium Ca isotope fractionation between calcite and aqueous Ca, we measured the Ca isotopic composition of pore fluids and calcite from sedimentary carbonate ooze deposits on the ocean floor. The results indicate that at equilibrium, the Ca isotopic ratios of calcite and coexisting dissolved Ca are

identical to within 0.002% per mass unit. When combined with observations from experiments and marine biogenic calcite, we find that this zero-fractionation condition occurs at both extremely slow and extremely fast rates of calcite precipitation. At intermediate rates, especially those applicable to biogenic calcite precipitation, there is fractionation that favors the incorporation of light isotopes into the precipitating solid. This behavior implies that the isotopic fractionation is heavily dependent on the kinetics of adsorptive attachment and detachment.

SIGNIFICANCE OF FINDINGS

The inference that isotopic fractionation is affected by attachment kinetics, in addition to equilibrium partitioning and diffusive transport, has far-reaching implications for understanding the chemical and isotopic composition of all natural materials. Not only is it important to be able to accurately describe the fractionations, but observed fractionations in natural materials may help to distinguish which processes are most active in their formation. A further challenge is to develop models that can predict isotopic fractionation based on the conditions of mineral growth from solution.

RELATED PUBLICATIONS

Fantle, M.S., and D.J. DePaolo, Ca isotopes in carbonate sediment and pore fluid from ODP Site 807A: The $\text{Ca}^{2+}(\text{aq})$ -calcite equilibrium fractionation factor and calcite recrystallization rates in Pleistocene sediments. *Geochim. Cosmochim. Acta*, doi: 10.1016/j.gca.2007.03.006, 2007.

ACKNOWLEDGMENT

This research was supported by the Director, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences and Biosciences Division of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231 to LBNL. Deep sea samples were obtained from the Ocean Drilling Program (ODP), which is sponsored by the U.S. National Science Foundation (NSF) and participating countries under management of Joint Oceanographic Institutions (JOI), Inc.

LATTICE BOLTZMANN SIMULATIONS OF SNOW CRYSTAL GROWTH

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RESEARCH OBJECTIVES

This study aims at simulating snow crystal growth—a vapor deposition process in clouds involving physics such as vapor diffusion, and reaction. Although it is known that crystal growth rate, which depends largely on the degree of vapor oversaturation, determines crystal morphology, there is no general model by which to relate morphology to vapor saturation. A numerical method capable of simulating the shape evolution of snow crystals is essential for interpreting relevant physics, effect of pollutants on snow formation, and isotope behaviors.

APPROACH

We use a 2-D lattice Boltzmann (LB) model to simulate diffusion-controlled snow crystal growth from vapor-oversaturated air. The vapor depositions were accommodated through both diffusion and reaction rates. The two-dimensional, nine-speed model of Kang et al. (2004) was modified to accommodate the specific boundary conditions needed. In the model, “crystals” grow solely according to the diffusive fluxes just above the crystal surfaces, and hence morphology arises only from the initial and boundary conditions. The effect of reaction relative to that of diffusion was described with the Damkohler number $Da = k_r h / D$, where k_r is the local reaction-rate constant, h is length dimension of the model domain, and D is the diffusivity.

ACCOMPLISHMENTS

We have successfully simulated the hexagonal symmetry of the snow growth (Figure 1). Our calculations demonstrate that crystal is a compact plate, and fractionation approaches the equilibrium value as the saturation factor approaches unity ($S = 1.0$). Also, at higher oversaturation (e.g., $S = 1.2$), millimeter-sized dendritic crystals develop over time scales appropriate to cloud processes. The results help clarify the controls on dendritic crystal growth, and the relationships between saturation state, growth rate, crystal morphology, and isotopic fractionation. They also show the extent to which crystals are likely to be isotopically heterogeneous.

SIGNIFICANCE OF FINDINGS

LB simulation connects the crystal growth processes and isotopic kinetic effects. The simulation results explain the isotopic variation in evaporation/condensation, snow and ice formation, and crystal growth. LB simulation provides a method for evaluating the fractionation of isotopes in natural systems and extends

the simulation capability for investigating the physics, bridging the molecular dynamics and conventional continuum domain.

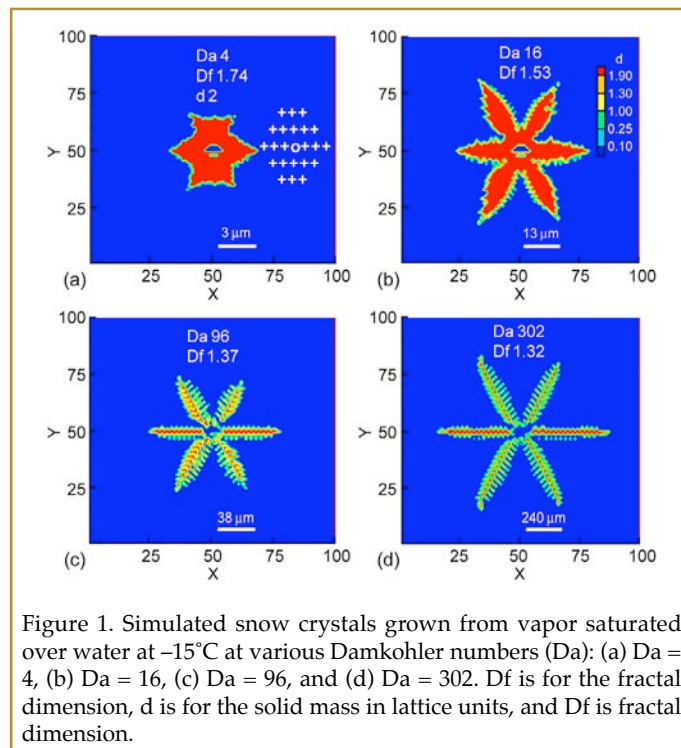


Figure 1. Simulated snow crystals grown from vapor saturated over water at -15°C at various Damkohler numbers (Da): (a) $Da = 4$, (b) $Da = 16$, (c) $Da = 96$, and (d) $Da = 302$. Df is for the fractal dimension, d is for the solid mass in lattice units, and Df is fractal dimension.

RELATED PUBLICATION

- Kang et al., Lattice Boltzmann model for crystal growth from supersaturated solution. *Geophys. Res. Lett.* 31, L21604, 2004.
- Lu, G., D.J. DePaolo, Q. Kang, and D. Zhang, Lattice Boltzmann simulation of snow crystal growth. *Water Resour. Res.*, 2007.
- DePaolo, D.J., and G. Lu, Kinetic isotope effects in snow crystal growth: Lattice Boltzmann approach. *J. Geophys. Res.*, 2007.

ACKNOWLEDGMENTS

This work was supported in part by the Laboratory Directed Research and Development (LDRD) from Berkeley Lab, provided by the Director, Office of Science, of the U.S. Department of Energy under Contract No. DE-AC03-76SF0098. We would like to thank Qijun Kang (Los Alamos National Laboratory) and Dongxiao Zhang (University of Southern California) for their support.

DEVELOPMENT OF JOINT HYDROLOGICAL-GEOPHYSICAL DATA INVERSION METHODOLOGY

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RESEARCH OBJECTIVES

The ultimate goal of most site characterization efforts is to understand and describe the main subsurface features in sufficient detail, so that a reliable prediction of fluid movement, contaminant transport, and biogeochemical reactions can be made. The challenge of characterizing the subsurface at a specific site lies in the fact that the soil structure is unknown and exhibits both random and nonrandom features—i.e., it cannot be adequately described using purely stochastic or purely deterministic approaches. In addition to identifying the geometry of the stratal soil architecture, hydrologic and geochemical parameters need to be assigned. The specific objective of this research is to develop a data analysis method that allows one to determine both the soil structure and related hydrologic parameters with adequate resolution for a given site.

APPROACH

The basic concept is to perform a joint analysis of geophysical data, which provide a high-resolution image of the subsurface, and hydrological data, which contain information about the flow and transport properties of interest. Moreover, geostatistical simulation methods are used to flexibly describe a heterogeneous soil structure with a limited number of parameters. Finally, a petrophysical model is needed to relate, for example, the fluid distribution in the subsurface to the geophysical signal. The parameters of such a petrophysical model are also considered unknown or uncertain, and are thus concurrently estimated. In summary, we simultaneously estimate hydrological, petrophysical, and geostatistical parameters by jointly inverting time-lapse hydrological and geophysical data.

ACCOMPLISHMENTS

The joint inversion approach as been implemented into the iTOUGH2 code (Finsterle, 2004; <http://www-esd.lbl.gov/iTOUGH2>) by linking geophysical modeling of ground penetrating radar (GPR) signals and geostatistical simulation to the already available nonlinear parameter estimation methods. An example of a synthetic infiltration experiment is shown in Figure 1, where a highly heterogeneous, anisotropic soil structure and its related properties are determined by the joint inversion of hydrological data (infiltration rates and water content data derived from neutron logging) and geophysical data (arrival times from a crosshole GPR survey).

SIGNIFICANCE OF FINDINGS

By dynamically adjusting the soil structure during the optimization process, the proposed approach significantly improves the model representation of subsurface heterogeneity, thus reducing the risk of substantial estimation and prediction errors. Moreover, the joint analysis of geophysical and hydrological data is a means to

characterize both the key features and relevant processes that affect subsurface flow and transport. The approach is expected to be valuable for analyzing other geophysical data types, such as electrical resistance tomography (ERT).

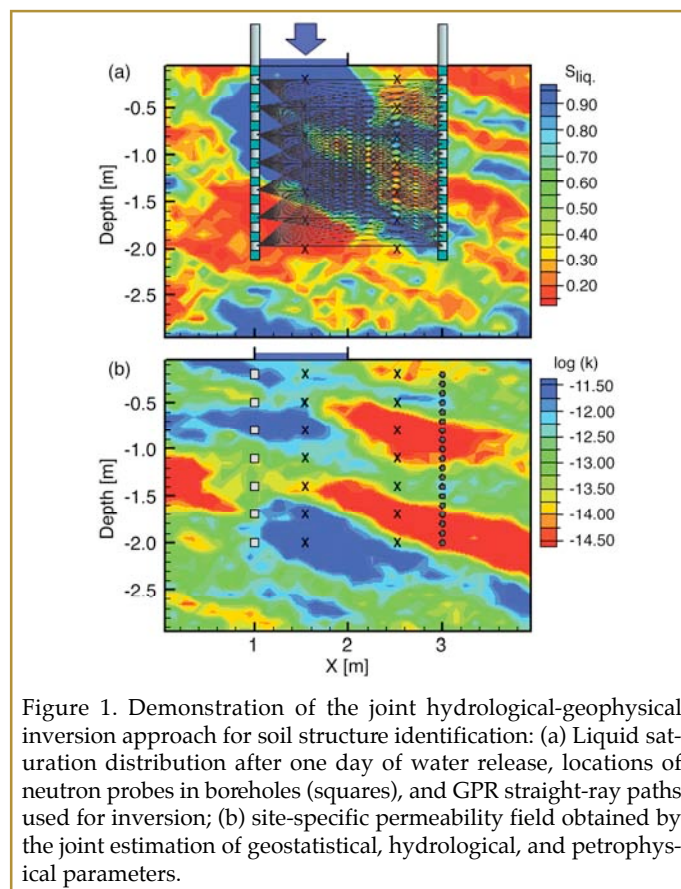


Figure 1. Demonstration of the joint hydrological-geophysical inversion approach for soil structure identification: (a) Liquid saturation distribution after one day of water release, locations of neutron probes in boreholes (squares), and GPR straight-ray paths used for inversion; (b) site-specific permeability field obtained by the joint estimation of geostatistical, hydrological, and petrophysical parameters.

RELATED PUBLICATIONS

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- Finsterle, S., and M.B. Kowalsky, Joint hydrological-geophysical inversion for soil structure identification. *Vadose Zone J.* (in press), 2007.
- Kowalsky, M., S. Finsterle, J. Peterson, S. Hubbard, Y. Rubin, E. Majer, A. Ward, and G. Gee, Estimation of field-scale soil hydraulic parameters and dielectric parameters through joint inversion of GPR and hydrological data. *Water Resour. Res.*, 41, W11425, doi:10.1029/2005WR004237, 2005.

ACKNOWLEDGMENTS

This work was supported by Laboratory Directed Research and Development (LDRD) funding from Berkeley Lab, provided by the Director, Office of Science, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

EFFECTS OF NANOPARTICLE AGGREGATION ON METAL ION ADSORPTION

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RESEARCH OBJECTIVES

Nanoscale oxide and oxyhydroxide minerals are commonly found in the natural environment and play important roles in adsorbing and sequestering aqueous ions, including nutrients such as phosphates and contaminants such as heavy metals. Upon formation, these materials are typically subjected to natural flocculation events that reduce the nanoparticle surface area accessible by aqueous ions. Our goal is to assess the effects of different kinds of aggregation processes on the morphology of nanoparticle aggregates and metal uptake by the mineral surfaces.

APPROACH

We synthesized a suspension of ~6 nm iron oxyhydroxide nanoparticles and subjected portions of this suspension to analogues of natural aggregation processes. These included: pH variation around the point of zero surface charge (simulating the neutralization of acid mine drainage), ionic strength elevation (simulating mixing of aquifer and brackish water), drying, and freezing. Following aggregation, each sample was returned to the initial control conditions (pH 5, 0.001 M ionic strength), without significant change in aggregation state. The effect of aggregation on metal ion uptake was studied by exposing batches of aggregated and control samples to 0.5 mM Cu(NO₃)₂ at pH 6.0 for 24 hours.

ACCOMPLISHMENTS

While all aggregation processes caused visual flocculation and settling, there were large quantitative differences in the impact on Cu uptake. Aggregation via pH or ionic strength variation caused a modest drop in uptake relative to nonaggregated nanoparticles, while freezing and drying processes resulted in significant reductions in uptake. Small-angle x-ray scattering (SAXS) data provide insight into aggregate morphology and permit the batch uptake experiments to be interpreted. In water, the nanoparticles form open fractal-like networks, characterized by relatively low values of geometric fractal dimension ($D_f \sim 1.4$). By contrast, drying or freezing force the nanoparticles into densely packed clumps of porous material. SAXS-based simulation techniques can generate representative morphologies of the aggregates.

SIGNIFICANCE OF FINDINGS

These findings illustrate the diverse nanoporous structures that can be generated by natural nanoparticle aggregation processes. In particular, they highlight the important role of water in preserving hydrated channels among aggregated nanoparticles that are permeable to aqueous ions.

RELATED PUBLICATIONS

Gilbert, B., G. Lu and C.S. Kim, Stable cluster formation in aqueous suspensions of iron oxyhydroxide nanoparticles. *J. Colloid Interf. Sci.*, 313, 152–159, 2007.

ACKNOWLEDGMENTS

Use of the Stanford Synchrotron Radiation Laboratory (SSRP) is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-AC02-05CH11231. Financial support for this work came from the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

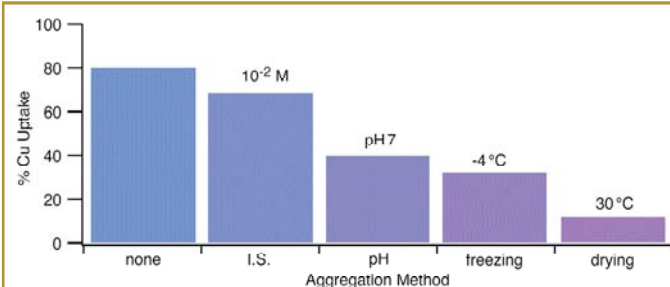


Figure 1. The proportion of Cu²⁺(aq.) adsorbed from solution onto FeOOH nanoparticles that were either fully suspended or aggregated via different mechanisms. I.S. = "ionic strength."

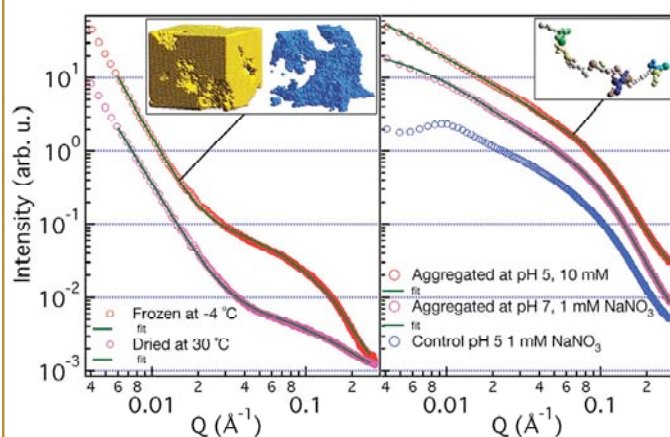


Figure 2. *In situ* small-angle x-ray scattering (SAXS) analysis of FeOOH nanoparticle aggregates in suspension (control), or aggregated. Fits to the experimental SAXS patterns permit representative aggregate morphologies to be generated (inset). Left inset: Pore structure of a compact nanoparticle aggregate generated by freezing. Brown = particle structure, blue = pore structure. Right inset: Structure of a fractal aggregate generated by increasing ionic strength.

NATURE'S SEMICONDUCTOR'S: ELECTRONIC STRUCTURE OF BIOGENIC MANGANESE OXIDES

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RESEARCH OBJECTIVES

Many bacteria produce Mn(IV) oxides (MnO_2), which are environmental nanoparticles having a layered structure. Biogenic Mn oxides are known to be key participants in both redox reactions and metal-scavenging in soil and aquatic environments. An important structural characteristic of the oxides is the presence of Mn(IV) cation vacancies, whose charge deficit is typically compensated by metal cations or protons (Villalobos et al., 2006). These vacancies have long been identified as strong adsorption sites for heavy metals, but they may also play an important role in redox biogeochemistry, particularly in photo-induced redox reactions occurring in natural waters. Because electronic structure is the key to understanding (photo) redox transformations, the objective of our research is to theoretically examine the electronic structures of Mn oxides, both with and without Mn(IV) vacancies.

APPROACH

Quantum mechanical (QM) calculations have advanced to the point where they can provide highly accurate electronic-structure information about solids without adjustable parameters. In our study, the electronic structures of Mn oxides were calculated for model MnO_2 nanoparticles using a version of CASTEP, one of the best known and most reliable QM codes in solid-state physics. These extensive calculations required the massively parallel supercomputing resources of the National Energy Research Scientific Computing Center (NERSC).

ACCOMPLISHMENTS

We investigated MnO_2 nanosheets containing Mn(IV) vacancies compensated by protons. Negative charge was found to be localized at the vacancy sites. Our results also demonstrated that increasing the Mn(IV) vacancy concentration effectively reduced the band-gap energy between the occupied valence band and the unoccupied conduction band of electrons in the Mn oxides (Figure 1). Thus, a Mn(IV) vacancy can facilitate photo-induced electron transfer

(redox reactions) between the oxide mineral and inorganic or organic compounds.

SIGNIFICANCE OF FINDINGS

Biogenic MnO_2 nanoparticles can serve as design templates for new materials. Recent research in materials science indicates that synthetic Mn oxide nanoparticles with layer structures and Mn(IV) vacancies like those in biogenic MnO_2 are semiconductors that produce photocurrents under visible light stimulation, thus making them attractive for applications in energy storage, solar cell fabrication, and catalysis. Understanding their electronic structure is essential to developing their full potential, and our QM results strongly imply that nanoparticle MnO_2 with Mn(IV) vacancies offers an effective new material for generating and transferring photo-induced electrons and holes. More specifically, the finding of substantial band-gap energy reduction by a vacancy suggests that photocurrent production by layer type MnO_2 can be optimized by the control of vacancy rates during synthesis.

RELATED PUBLICATIONS

Villalobos, M., B. Lanson, A. Manceau, B. Toner, and G. Sposito, Structural model for the biogenic Mn oxide produced by *Pseudomonas putida*. *American Mineralogist*, 91, 489–502, 2006.

Kwon, K.D., K. Refson, and G. Sposito, Ruetschi defects decrease the band gap energy in MnO_2 nanosheets. *Journal of American Chemical Society* (in press), 2007.

ACKNOWLEDGMENTS

This research was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. Our computations used resources of the National Energy Research Scientific Computing Center (NERSC) at Berkeley Lab, which is also supported by DOE Contract No. DE-AC02-05CH11231.

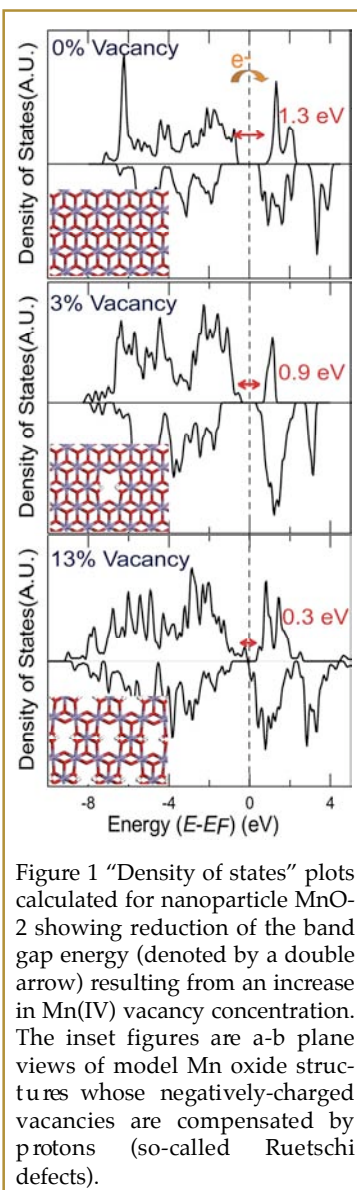


Figure 1 "Density of states" plots calculated for nanoparticle MnO_2 showing reduction of the band gap energy (denoted by a double arrow) resulting from an increase in Mn(IV) vacancy concentration. The inset figures are a-b plane views of model Mn oxide structures whose negatively-charged vacancies are compensated by protons (so-called Ruetschi defects).

CO₂-H₂O MULTIPLE PHASE AND COMPONENT SIMULATION: A LATTICE BOLTZMANN APPROACH

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RESEARCH OBJECTIVES

Global warming from burning of fossil fuels has generated an increasing interest in the study of carbon dioxide's geological sequestration. Sequestration of CO₂ into deep aquifers has been identified as a suitable route for mitigating CO₂ released to the atmosphere. However, the permanency of such storage is a concern. When compressed CO₂ is injected into aquifers, it is not in chemical equilibrium with the subsurface environment; it is buoyant, and therefore has the potential to migrate back to the surface through fissures in formation cap rock or along well bores. Compressed carbon dioxide—a nonwetting fluid of limited solubility in water—evolves as it interacts with water and with solid matrix in the subsurface. The objective of this study is to investigate the interaction between CO₂ and water.

APPROACH

We used 2-D and 3-D lattice-Boltzmann (LB) models to simulate dissolution of CO₂ in water. The two-dimensional, nine-speed model of Kang et al. (2002) was modified to accommodate multiple components and specific boundary conditions. In the model, the phase transition and solid interactions in porous media were accommodated through interfacial tensions.

ACCOMPLISHMENTS

We have successfully simulated the mutual dissolution of CO₂ in water (Figure 1) under different supercritical conditions—with interfacial tension dropping under increased pressures. The model was calibrated with laboratory-measured interfacial tension data from the relevant literature. Results show that both CO₂ and water might exist as isolated phases trapped within pores.

SIGNIFICANCE OF FINDINGS

LB simulation of CO₂-H₂O-solid interfacing is a new approach for the study of CO₂ behavior in geological sequestration. Our microscale simulation provides insight into CO₂ behavior, which can be validated by micro-imaging of the CO₂-water-rock system. The multiphase flow problem in porous

media is applicable to a wide range of practical problems, including heterogeneity and biopolymer surfactant issues in oil recovery, and the transport of nonaqueous-phase liquid contamination. The LB model can also be extended to study isotopic fractionation associated with storage of CO₂ in aquifers.

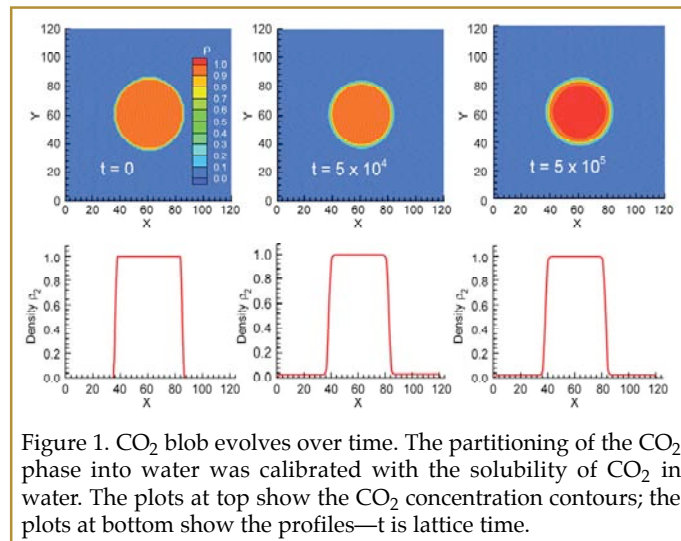


Figure 1. CO₂ blob evolves over time. The partitioning of the CO₂ phase into water was calibrated with the solubility of CO₂ in water. The plots at top show the CO₂ concentration contours; the plots at bottom show the profiles— t is lattice time.

RELATED PUBLICATION

Kang et al., Displacement of a 2-D immiscible droplet. *Physics of Fluids*, 14, 2002.

Lu, G., D.J. DePaolo, Q. Kang, and D. Zhang, Lattice-Boltzmann simulation of CO₂-water interaction in porous media. *Water Resources Research* (submitted), 2007.

ACKNOWLEDGMENTS

This work was supported by in part by Laboratory Directed Research and Development (LDRD) funds from Berkeley Lab, provided by the Director, Office of Science, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. We would like to thank Qinjun Kang (Los Alamos National Laboratory) and Dongxiao Zhang (University of Southern California) for their support of this work.

SHAPED-CORE UNIAXIAL COMPRESSION TEST FOR STUDYING BOREHOLE BREAKOUT IN ROCK

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RESEARCH OBJECTIVES

Borehole breakout in rock occurs as a result of stress concentration on a borehole wall subjected to far-field stresses. If the far-field stress is anisotropic, the highest stress concentration results in the directions corresponding to the minimum principal stress within a plane perpendicular to the borehole axis. To examine the effect of stress concentration on the formation of a borehole breakout, a “hollow-cylinder” test is conducted routinely, which applies an axisymmetric confining stress and an axial stress on a cylindrical rock sample containing a single hole along its axis. For more general, anisotropic stress states, a cube-shaped rock sample containing an analogue borehole is subjected to polyaxial stresses in the laboratory. The objective of this research is to develop an even simpler testing method for studying borehole breakout—as simple as a uniaxial compression test.

APPROACH

The shaped-core uniaxial compression (SCUC) test developed in this research potentially provides a very simple means by which to examine borehole breakout in rock. This method employs a cylindrical rock core with a narrowed cross section at the center (i.e., a “shaped” core), which gives the core an appearance of an

hourglass or dogbone (Figure 1). The same sample geometry has been used to test rock and metal samples for their tensile and extensile strengths. When a shaped core is subjected to axial compression, the curved surface results in a stress concentration at the core wall, analogous to a real borehole subjected to far-field stresses. Laboratory experiments and numerical simulations using finite element models were conducted for a range of core geometry and material properties to examine the resulting stress distribution and borehole breakout.

ACCOMPLISHMENTS

SCUC tests were conducted on a variety of small rock samples (diameter=5.08 cm, height=5.08 cm), ranging from very friable, weakly cemented sand to extremely strong carbonate rock. This method was also used extensively to examine how fluid flow around a borehole affects sand production from a borehole breakout. Initial experiments and elastic stress analyses indicated that to model the behavior of a borehole adequately, a formation of tensile zone within a shaped core must be avoided by applying constraints at the top and bottom of a core.

SIGNIFICANCE OF FINDINGS

Unique advantages of the method were identified through the development of the SCUC test. These are (1) only a small sample is needed for the test, (2) both very weak and very strong samples can be tested easily, (3) an initiation and development of a borehole breakout can be visually and continuously observed, and (4) since no confining cell is needed, fluid can be circulated around the breakout within a transparent shell, to study sand production. However, it was also found that the stress concentration within a sample varies as a function of the core geometry and material properties.

ACKNOWLEDGMENTS

This work was supported by the Assistant Secretary for Fossil Energy, Office of Oil and Natural Gas, National Energy Technology Laboratory, and by Laboratory Directed Research and Development (LDRD) funding from Berkeley Lab, provided by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

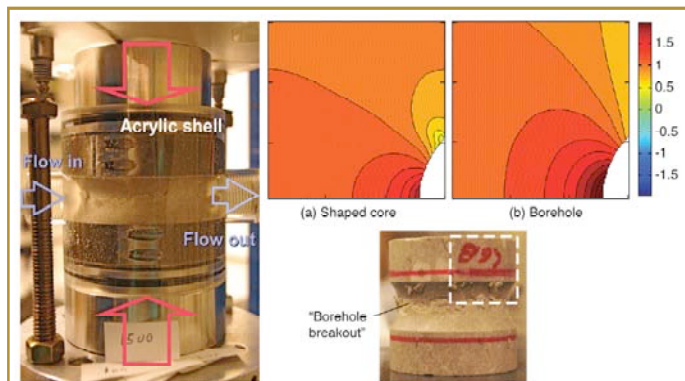


Figure 1. A shaped-core uniaxial compression test. An hourglass-shaped rock core is compressed to produce a stress concentration on the core wall, resulting in a local failure analogous to a borehole breakout. Vertical compressional stresses are compared in the plots (Normalized for the axial stress (a) and far-field vertical stress (b)). The ratio between the far-field vertical and horizontal stresses in (b) is 2:1.

PHYSICOCHEMICAL CONTROLS ON UNSATURATED FLOW AND TRANSPORT IN GEOLOGICAL MEDIA

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RESEARCH OBJECTIVES

The flow of water and transport of chemicals through soils and fractured rocks is strongly dependent on the water content (saturation), with very low flow and transport rates occurring at low saturation levels. Under conditions in which both air and water occupy pores (fractures), water films largely control macroscopic flow and chemical transport. However, some basic properties of water films in unsaturated media remain poorly understood. The environmentally important characteristics being investigated in this study are the dependence of water film thickness on capillary (matric) potential and water film's possible dependence on major ion chemistry.

APPROACH

Capillary potentials on water films coating mineral surfaces (smooth as well as rough) are controlled by equilibration with aqueous salt solutions, under regulated subatmospheric pressures in a small suction plate chamber. The chamber is placed in front of an x-ray beam (National Synchrotron Light Source X26A, and Advanced Photon Source 13-IDC) used to determine film thicknesses through x-ray fluorescence of monovalent (Rb⁺ and Br⁻) and divalent (Ca²⁺ and SeO₄²⁻) ions in the water films. These hard x-ray synchrotron sources are necessary for efficient x-ray fluorescence monitoring of ionic tracers in water films within sealed environmental control chambers. The measurements on flat mineral surfaces provide information on limiting conditions for unsaturated flow and transport, and also test various equilibrium models for adsorbed water film thickness. The experiments on microscopically rough surfaces, including natural fracture surfaces, test the capillary film flow models.

ACCOMPLISHMENTS

Measurements of average film thicknesses and film transmissivities have been completed on several natural rough fracture surfaces. The most recent experiments have focused on basic measurements on flat quartz glass surfaces at very-near-zero matric potentials. We have successfully measured water films as thin as 90 nm using this method, and our calibration tests indicate that resolution of about 20 nm is achievable. The measured film thickness-potential trends (Figure 1) are qualitatively in agreement with an early model derived by Irving Langmuir, but the data are indicative of generally thicker films. A predicted ion-valence film-thickness dependence is being tested through comparisons of systems containing RbBr versus CaSeO₄ and MgSeO₄ solutions.

SIGNIFICANCE OF FINDINGS

Water films in the range of tens to hundreds of nanometer thickness are common in unsaturated soils and rocks, yet have previously been inaccessible to direct measurements. This new approach is allowing direct quantification of unsaturated

transport properties within water films under environmentally relevant conditions, including physicochemical influences on unsaturated hydraulic properties.

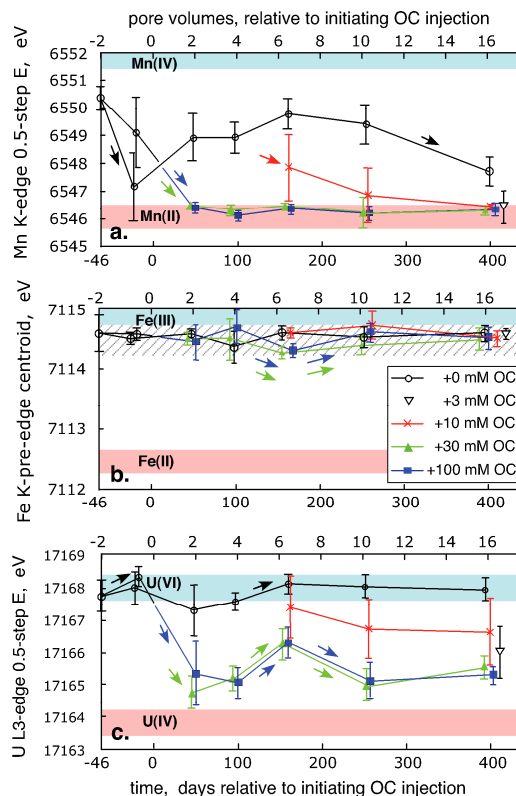


Figure 1. Comparisons between measured RbBr water film thicknesses on quartz glass, and predictions based on the Langmuir model, for a 1:1 solution.

RELATED PUBLICATION

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ACKNOWLEDGMENTS

This project is supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, of the U. S. Department of Energy under Contract No. DE-AC02-05CH11231. Use of the Advanced Photon Source and National Synchrotron Light Source was also provided by DOE under Contract No. DE-AC02-05CH11231.



MOLECULAR-LEVEL STUDIES OF MINERAL-WATER INTERFACE STRUCTURE AND CHEMISTRY

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RESEARCH OBJECTIVES

We wish to define the specific molecular geometries of mineral surfaces equilibrated with aqueous solutions, including the nature of surface relaxations or reorganizations, the attachment sites and type of binding of sorbates, and the structure of interfacial water. This type of information is important for the testing of molecular reaction models and simulation techniques that model the sorption/desorption and incorporation of migrant species in natural fluids, and hence determine the fate and transport of both toxic and nutrient species in the environment.

APPROACH

Our studies are conducted using a combination of molecular probes, largely synchrotron-based, with relatively simplified model systems. The chief synchrotron methods are: surface diffraction, by which we can refine the position and occupation of surface atoms at an interface; surface x-ray spectroscopy, by which we can obtain specific structural information about the local molecular environment of a sorbed molecule at an interface; and nonlinear optical spectroscopy, whereby we can probe the infrared vibrational spectrum of water molecules only at the solid-aqueous solution interface. Variations on these techniques also yield specific information such as the redox state of surface atoms, or the lifetimes of particular surface species.

ACCOMPLISHMENTS

Our most recent work focuses on the hematite, goethite, diasporite and corundum surfaces. For hematite, we are interested in the surface produced by acids or bases, as well as the geometry of sorbed species like arsenate or silicate. Results have shown that the geometry of monomeric silicate sorption is as a bidentate complex with strong surface attachment. The topology is such that silicate polymerization on the hematite surface (we investigated the R-plane) is likely, thus rendering the surface passivated to further reaction. For the goethite surface we were able to collect x-ray surface scattering data from submillimeter cleaved crystal fragments, and refine the surface

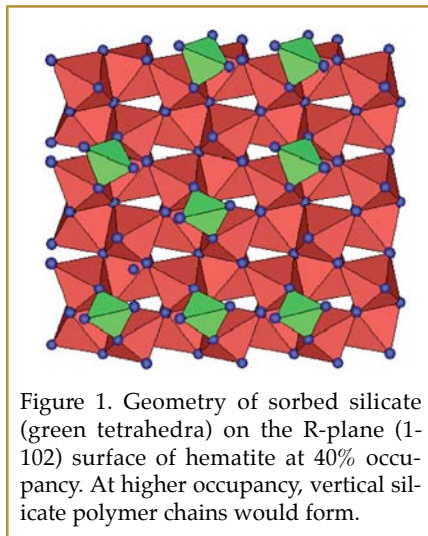


Figure 1. Geometry of sorbed silicate (green tetrahedra) on the R-plane (1-102) surface of hematite at 40% occupancy. At higher occupancy, vertical silicate polymer chains would form.

structure for the first time. The surface is relaxed from the bulk, but also has two distinct layers of ordered water at the termination. Analogous surface refinements are in progress for the aluminum-analog of goethite—diasporite. Our surface water studies show that the pH point of zero charge (PZC) for clean corundum (0001) faces is ca. 5.5, rather than the ca. 9.0 measured for corundum powders. This points to a basic misunderstanding of the aluminate-water surface interaction, which we are addressing with further studies of the corundum-water surface structure as a function of pH, as well as with MD simulations.

SIGNIFICANCE OF FINDINGS

The silicate/hematite work is vital to an understanding of how the reactivity of natural Fe oxide surfaces changes in varied environments, and whether effective remediation approaches for particular pollutants are efficacious. The goethite and diasporite work are crucial to the application of surface complexation modeling with accurate molecular parametrization. For example, current models assume bulk-goethite-like structure for the interface, which we show is not accurate. The PZC work shows fundamental problems with our solid-aqueous interface modeling assumptions, even in simple systems, but does yield new information by which we may be able to improve future molecular models.

RELATED PUBLICATION

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ACKNOWLEDGMENTS

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

NANOPARTICLE REACTIVITY, STRUCTURE, AND GROWTH STUDIES

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RESEARCH OBJECTIVES

Our past work has shown that nanoparticles differ in structure and strain, depending on their precise chemical environment. It is also anticipated that structure, strain, and reactivity may change as a function of size. Our investigations aim to characterize possible differences in sorption mechanisms as a function of nanoparticle size, growth rate, and degree of aggregation.

APPROACH

Our studies are done using a combination of molecular probes, bulk measurements, and thermodynamic measurements. Some of the analysis is done in concert with molecular dynamic simulations. For nanoparticle size and shape, we employ small angle x-ray scattering (SAXS) and dynamic light scattering (DLS), while the specific molecular nature of surface species is determined with extended x-ray absorption fine structure spectroscopy (EXAFS). Other aspects of nanoparticle structure are determined via determination of pair correlation functions with high-energy wide angle x-ray scattering (WAXS). The x-ray measurements are done at the APS (Advanced Photon Source) and SSRL (Stanford Synchrotron Radiation Laboratory) synchrotron sources.

ACCOMPLISHMENTS

Recent work shows that nanoparticle uptake of many types of sorbants is very high, initially, reflecting the large surface-to-volume ratio. In general, the numbers of active surface sites that sorb aqueous species do not seem to markedly increase in nanoparticles relative to larger particles, and in some cases are observed to decrease. This may result from a high degree of surface strain, manifested by surface site distortion, and thus somewhat disfavored geometries for strong covalent binding of sorbates. Growth of nanoparticles is also affected by sorption, with effects proportional to the strength of the binding and hence the degree to which nanoparticles can aggregate or grow by Ostwald ripening. Nanoparticle growth mechanisms in iron oxyhydroxides appear to occur by both oriented attachment (OA) and ripening mechanisms.

SIGNIFICANCE OF FINDINGS

An important mechanism for the uptake of natural pollutants by nanoparticles is incorporation by growing surfaces or

via aggregation mechanisms. We have shown that growth is highly sensitive to sorption of particular species, and hence that the fate and transport of environmental toxics is related in a complex manner to the size distribution of nanoparticles and the precise chemistry of sorbing species. For example, nanoparticles at smallest sizes may transport sorbed species for long distances without aggregation or growth if sorption densities are high. However the same particles would tend to aggregate or continue growth at low sorption densities, thus encapsulating the pollutants but with very limited transport.

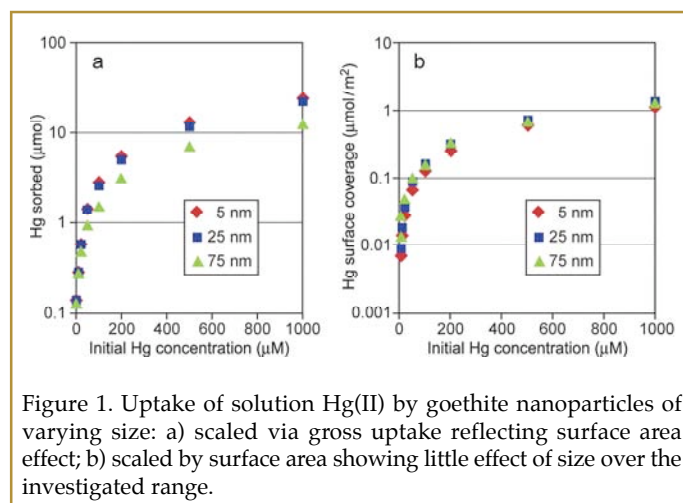


Figure 1. Uptake of solution Hg(II) by goethite nanoparticles of varying size: a) scaled via gross uptake reflecting surface area effect; b) scaled by surface area showing little effect of size over the investigated range.

RELATED PUBLICATIONS

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- Waychunas, G.A., C. Kim, and J.F. Banfield, Nanoparticulate iron oxide minerals in soils and sediments: Unique properties and contaminant scavenging mechanisms. *J. Nanoparticulate Res.*, 7, 409-433, 2005.

ACKNOWLEDGEMENTS

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

INCORPORATION OF AQUEOUS REACTION KINETICS AND BIODEGRADATION INTO TOUGHREACT

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RESEARCH OBJECTIVES

The need to consider aqueous and sorption reaction kinetics and microbiological processes arises in many subsurface problems. By adding these process-modeling capabilities to the TOUGH family of codes, complex problems can be addressed that involve multiphase fluid and heat flow, and biologically mediated geochemical interactions.

APPROACH

A general formulation for kinetic rates among chemical and microbial species has been incorporated into the reactive geochemical transport simulator TOUGHREACT. The space discretization used is based on a flexible integral finite difference approach that uses irregular gridding to model small-scale biogeologic regions and structures. A general multiregion model for hydrological transport coupled with microbiological and geochemical processes is used (Figure 1).

ACCOMPLISHMENTS

A 1-D reactive transport problem with kinetic biodegradation and sorption was used to test the enhanced simulator, which involves the processes that occur when a pulse of water containing NTA (nitrilotriacetate) and cobalt is injected into a column. The current simulation results agree very well with those obtained with other simulators. The applicability of this general multiregion model was validated by results from a published column experiment of denitrification and sulfate reduction. The matches with measured nitrate and sulfate concentrations were adjusted with the interfacial area between mobile and immobile regions (Figure 1). Results suggest that TOUGHREACT not only can be a useful interpretative tool for biogeochemical experiments, but also can produce insight into processes and parameters of coupled advective and diffusive transport, and their interplay with biogeochemical reactions.

SIGNIFICANCE OF FINDINGS

The resulting biogeochemical-transport-simulation capabilities may be useful for both deep and shallow subsurface problems, including acidic mine drainage remediation, biologically enhanced CO₂ sequestration, microbially enhanced oil recovery, and environmental remediation of groundwater contamination. This new capability is finding immediate application to studies of nitrogen cycling in the shallow subsurface and its coupling to hydrologic and climatologic forcings through a joint Earth Sciences Division and Berkeley Water Center project.

RELATED PUBLICATIONS

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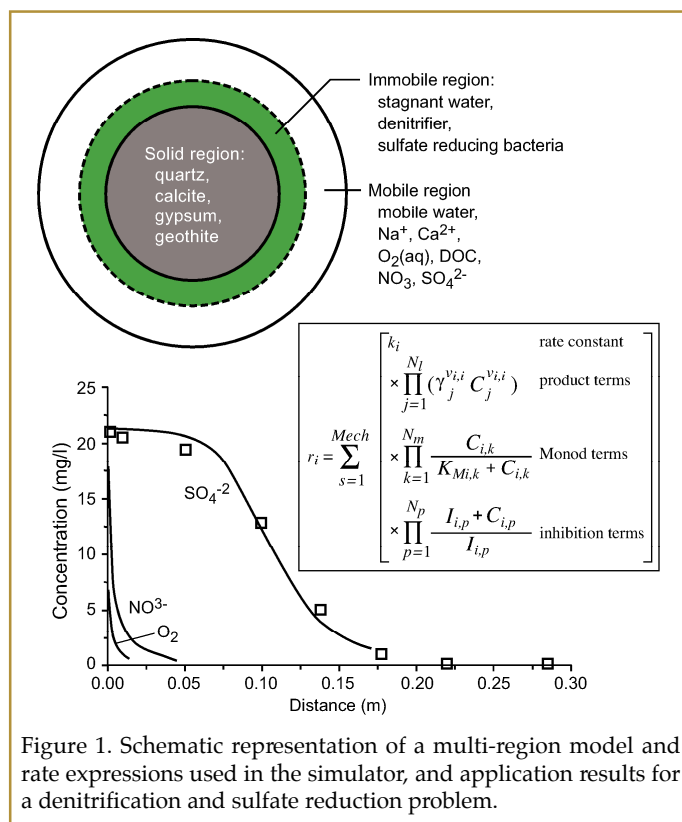


Figure 1. Schematic representation of a multi-region model and rate expressions used in the simulator, and application results for a denitrification and sulfate reduction problem.

ACKNOWLEDGMENTS

This work was supported by Laboratory Directed Research and Development (LDRD) funding from Berkeley Lab, provided by the Director, Office of Science, Office of Basic Energy Science, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

